

1034,197



## PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

**Sulphonic Acid Derivatives of Fluorocarbon Vinyl Ethers, and Polymers thereof**

We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organized and existing under the laws of the State of Delaware, United States of America, of Wilmington,

5 State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to novel fluorocarbon vinyl ethers and polymers thereof.

According to the present invention we provide fluorocarbon vinyl ethers of the formula

15  $\text{MSO}_2\text{CFR,CF}_2\text{O}[\text{CFYCF}_2\text{O}]_n\text{CF}-\text{CH}_3$ ,

where  $\text{R}_1$  is fluorine or a perfluoroalkyl radical having from 1 to 10 carbon atoms, Y is fluorine or the trifluoromethyl radical, n is

20 1, 2 or 3, and M is fluorine, a hydroxyl radical, an amino radical or a radical having the formula —OMet where Met is an alkali metal or a substituted or unsubstituted ammonium radical.

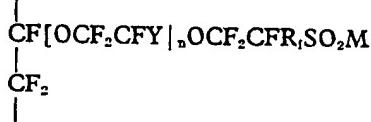
These vinyl ethers are readily homopolymerized or copolymerized with ethylene or halogenated ethylenes. Although these ethylenes are the preferred comonomers for the copolymerization of the vinyl ethers of the present invention, it is to be understood that 25 copolymerization of the vinyl ethers can be achieved with any ethylenically unsaturated comonomer capable of homopolymerization, using the polymerization techniques described hereinbelow.

[P]

Preferred copolymers derived from two monomers are those obtained from fluorocarbon vinyl ethers according to the invention in which  $\text{R}_1$  is fluorine, Y is a trifluoromethyl radical and n is 1, and tetrafluoroethylene. 35

Additional fluorinated monomers may also be copolymerized with ethylene or halogenated ethylenes and the fluorocarbon vinyl ethers of the present invention. In particular, a perfluoro(alkyl vinyl ether) or a perfluoro alphaolefin is a preferred third monomer for copolymerization. 40 45

The polymers obtained by homopolymerization or copolymerization of the fluorocarbon vinyl ethers according to the invention contain structural units of the formula



where  $\text{R}_1$ , Y, n and M have the above-stated meanings.

The solid products produced by copolymerization using the vinyl ethers of the present invention may be plastic or elastomeric. If elastomeric products are desired, the fluorocarbon vinyl ethers of the present invention can be polymerized in combination with two or more other monomers to produce multi-component copolymers. 55 60

In these polymers it is generally preferred that at least one of the additional monomers be ethylene or a halogenated ethylene such as

vinylidene fluoride, tetrafluoroethylene, or chlorotrifluoroethylene, while the other additional monomer is a perfluoro(alkyl vinyl ether) of the type



wherein n is 0 to 5, inclusive.

The concentration of fluorocarbon vinyl ethers of the present invention which contain sulfonic acid groups or derivatives thereof is

chosen in relation to the degree of cross-linkability desired for the copolymer product. For economic reasons, 5 mole per cent, based on total monomer incorporated into the copolymer, is usually all that is used to produce high modulus vulcanized products, while 0.2 mole per cent is about the minimum which will produce a satisfactory degree of crosslinking. For example, when copolymers are prepared from vinylidene fluoride, hexafluoropropylene and a perfluorovinyl ether of the structure

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good elastomers are obtained when the molar ratio of vinylidene fluoride to hexafluoropropylene lies within the range of 51:49 to 85:15 and the proportion of the fluorocarbon vinyl ether is present in the range of about 0.2 mole to 5 mole per cent of the total monomer units

present in the copolymer.

In the preparation of elastomeric copolymers from tetrafluoroethylene, perfluoro(methyl vinyl ether) and a perfluorovinyl ether of the structure

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a preferred range of molar ratios is 1.5-2.0 moles of tetrafluoroethylene per mole of perfluoro(methyl vinyl ether) with 0.5-4 mole per cent of the total composition of the sulfonyl fluoride monomer.

The vinyl ethers of the present invention in which M is fluorine can be prepared by the pyrolysis of compounds having the following formulae

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35  $FSO_2 CFR, CF_2 O [CFYCF_2 O]_n CF(CF_3) COF$   
and  
45  $FSO_2 CFR, CF_2 O [CFYCF_2 O]_n CF(CF_3) COOX,$

50 where R, Y and n have the same meaning as above and X is an alkali metal. The pyrolysis is carried out at temperatures of 180° to 600°C. In the case of the carboxylic acid fluoride, silica or a metal oxide such as zinc oxide is preferably employed as a solid catalyst for the gas phase reaction. The carboxylic acid fluoride employed in the pyrolysis is obtained by the reaction of hexafluoropropylene epoxide with a fluorosulfonyl fluoroacyl fluoride having the formula

55 aqueous solution of ammonia, and the salts, i.e. the compounds in which M is —OMet, can be obtained by salifying the sulphonic acid compounds with an alkali metal compound or an ammonium or substituted ammonium compound as appropriate. All these reactions can be carried out under mild conditions, usually room temperature, and no catalyst is required.

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60 The vinyl ethers of the present invention are preferably polymerised in a perfluorocarbon solvent using a perfluorinated free radical initiator. Since the vinyl ethers are liquid at reaction temperatures, it is further possible to polymerize and copolymerize the vinyl ethers in bulk without the use of a solvent. It is preferable to polymerize the vinyl ether in the form of the sulfonyl fluoride when using a perfluorocarbon system. Polymerization temperatures will vary from -50 to +200°C depending on the initiator used. Pressure is not critical and is generally employed to control the ratio of the gaseous comonomer to the fluorocarbon vinyl ether. Suitable fluorocarbon solvents are known in the art and are generally perfluoroalkanes or perfluorocycloalkanes, such as perfluoroheptane or perfluorodimethylcyclobutane. Similarly, perfluorinated initiators are known in the art and include perfluoroperoxides and nitrogen fluorides.

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65 In the form of the acid or the acid salt 105

70 The alkali metal salt of the carboxylic acid is formed from the corresponding acid fluoride by reaction with an alkali metal salt of a weak acid, such as carbonic acid. The formation of the acid fluoride and the alkali metal salt is further disclosed in copending application No. 31,684/64 (Serial No. 1034196).

75 The vinyl ethers in which M is fluorine obtained by pyrolysis as described above can be readily converted into the corresponding compounds in which M is a hydroxyl radical, an amino radical or a radical of the formula —OMet. The sulphonic acid compounds, i.e. those in which M is —OH, can be obtained by hydrolysis with water, the sulphonic acid amide compounds, i.e. those in which M is —NH<sub>2</sub>, can be obtained by treatment with an

the fluorocarbon ethers of the present invention can be polymerized in an aqueous medium using a free radical initiator, that is a peroxide or a redox initiator and this type of polymerization can also be used, if desired, with the sulphonyl fluoride fluorocarbon ethers. The polymerization methods employed correspond to those established in the art for the polymerization of tetrafluoroethylene in aqueous media.

In preparing copolymers using the fluorocarbon vinyl ethers of the present invention, it is generally preferred to use aqueous media at a pH of 8 or lower and temperatures not above about 110°C.

The polymeric fluorocarbon vinyl ethers of the present invention are liquid or solid depending on their degree of polymerization. The sulfonyl group in the polymer is readily subjected to known reactions of sulfonyl groups and can thus be employed to form a variety of polymeric sulfonyl group containing materials.

Copolymers containing the fluorocarbon vinyl ethers of the present invention can be vulcanized using the  $-\text{SO}_2\text{F}$  group or derivatives thereof, such as the  $-\text{SO}_2\text{OH}$  or  $-\text{SO}_3\text{Na}$  groups, by heating in the presence of metal oxides such as  $\text{PbO}$  or mixtures of  $\text{PbO}$  and  $\text{MgO}$ , or by reacting with polyfunctional reagents capable of reacting with sulfonyl fluorides, such as diamines.

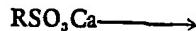
The polymeric vinyl ethers of the present invention which find utility as plastics can be molded or extruded into a variety of shapes. Of particular utility are aqueous dispersions of the vinyl ether polymer in which the vinyl ether contains an  $-\text{SO}_3\text{Na}$  group. These dispersions have the appearance of an aqueous syrup and are homogenous and transparent and may even contain the polymer in solution. The dispersions can be employed to coat metals and other surfaces and form coherent and contin-

uous coatings without the requirement of sintering or melting the polymer. Such coatings are not redissolved or redispersed by prolonged contact with water. In this respect the polymers of the present invention differ from prior art fluorocarbon polymers all of which require sintering or melting to give rise to coherent coatings.

The polymeric vinyl ethers of the present invention which are useful as elastomers offer desirable combinations of properties such as heat resistance, chemical stability, and resistance to attack by many fluids which are used industrially such as those contained in hydraulic systems, dry - cleaning solvents and aircraft fuels.

The preparation of elastomeric products, such as seals, gaskets and grommets, using the polymeric vinyl ethers, follows technology which is conventional for other fluoroelastomers, i.e., various fillers may be compounded into the polymers by milling, followed by moulding under heat and pressure into various useful articles.

The polymeric vinyl ethers of the present invention are furthermore highly useful as ion exchange resins in that they contain sulfonyl groups. Thus, the resins can undergo exchange cycles, e.g.,

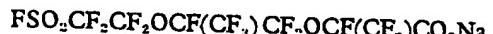


$\text{RSO}_3\text{H}$  by use of common reagents. The resins in their acid form can also be used as acid catalysts at elevated temperatures.

The invention is further illustrated by the following examples.

#### EXAMPLE I

Into a rotary evaporator was charged 200 g of



The evaporator was heated to 180°C until no further gas evolution was observed. The off-gases from the reaction were condensed in a cold trap. On distillation, there was obtained

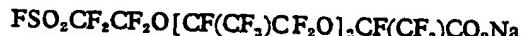
48 g of perfluoro[2-(2-fluorosulfonylethoxy)propyl vinyl ether], b.p. 118°C. The infrared and NMR spectra of the product were consistent with the structure of the ether.

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Anal. Calcd. for  $\text{C}_{14}\text{F}_{14}\text{O}_5\text{S}$  : C, 18.84; F, 59.62; S, 7.18.  
Found : C, 19.11; F, 59.13; S, 7.11.

#### EXAMPLE II

Into a rotary evaporator was charged 150 g of



The evaporator was heated to 200°C until no further gas evolution was observed. The off-gases from the reaction were condensed

in cold traps. On distillation of the reaction product there was obtained 35 g of

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having a boiling point at 159°C. Infrared and NMR spectra was consistent with the indicated structure.

**EXAMPLE III**

The fluorosulfonyl fluoroacyl fluoride, having the formula



was passed through a one inch stainless steel column packed with 1/4 inch pellets of ZnO and heated to a temperature of 285°C. The fluorosulfonyl fluoroacyl fluoride, 85 g, was vaporized by dripping on a flash evaporator in a nitrogen stream of 400 ml/min. The nitrogen stream was then passed through the column and multiple cold traps in which the reaction product was collected. Upon separation, there was obtained 60 g of the perfluoro [2 - (2 - fluorosulfonylethoxy)propyl vinyl ether].

**EXAMPLE IV**

The procedure of Example III is repeated using a spherical glass beads (200 to 325 mesh) at a temperature of 325°C instead of

**EXAMPLE VII**  
Using the procedure of Example VI, the vinyl ether having the formula



is polymerized to a clear viscous homopolymer.

**EXAMPLE VIII**

Into an evacuated 320 ml stainless steel shaker tube were charged 40 g of the vinyl ether,



40 g of tetrafluoroethylene and 200 ml of perfluorodimethylcyclobutane. While cold, a 30 ml jumper line was pressured to 20 psig with 2.4 volume per cent difluorodiazine in nitrogen. This catalyst was pressured into the shaker tube with 800 p.s.i. of nitrogen. The mixture was shaken and the temperature raised slowly to 80°C and maintained there for one hour. On cooling and discharging, 28 g of 9 weight per cent vinyl ether copolymer having melt viscosity above  $1 \times 10^3$  poises was obtained. The polymer could be compression molded into clear tough film.

**EXAMPLE IX**

Into an evacuated 320 ml stainless steel shaker tube were charged 30 g of purified vinyl ether having the formula

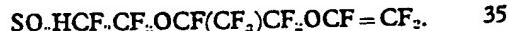


200 ml of deoxygenated, distilled water, about

ZnO and a temperature of 285°C. Yields of the perfluorovinyl ether of up to 80% are obtained.

**EXAMPLE V**

Perfluoro [2 - (2 - fluorosulfonylethoxy) - vinyl ether] was dissolved in an alkaline acetone water mixture which resulted in the formation of the corresponding sodium salt. The isolated salt was treated with a concentrated solution of HCl to form the corresponding sulfonic acid



Reaction of the sulfonic acid ether with aqueous sodium hydroxide or triethylamine resulted in the formation of the corresponding pure sodium salt or triethyl ammonium salt.

**EXAMPLE VI**

About 0.5 g of perfluoro [2 - (2 - fluorosulfonylethoxy) propyl vinyl ether] is placed in a quartz tube which is then evacuated and sealed. After 24 hours irradiation with a mercury arc lamp, a clear viscous homopolymer is obtained.

**EXAMPLE VII**

Using the procedure of Example VI, the vinyl ether having the formula

30 g of tetrafluoroethylene and 1.0 g of ammonium persulfate. The reaction mixture was heated under autogenous pressure to 68-70°C for 2 hours. On discharging 48 g of gelatinous copolymer was obtained which after drying could be made into films of good stiffness and contained 14 weight per cent of the vinyl ether.

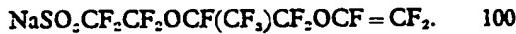
**EXAMPLE X**

Into an 85 ml stainless steel shaker tube were charged 60 ml of deoxygenated distilled water, 0.3 g of dry ammonium persulfate, 2.5 g of a vinyl ether having the formula



and 6 to 10 g of tetrafluoroethylene. The mixture was agitated at 68°C for 3 hours under autogenous pressure and a clear aqueous copolymer dispersion was discharged.

The procedure is readily employed with other ethylenes, such as chlorotrifluoroethylene, vinylidene fluoride, vinyl fluoride, vinyl chloride, vinylidene chloride and ethylene to give rise to aqueous dispersions of copolymers of these ethylenes with



**EXAMPLE XI**

To 100 ml of a 50 weight per cent aqueous NaOH solution and 100 ml of methanol is added 60 g of a copolymer of tetrafluoroethylene and

- 5  $\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF} = \text{CF}_2$ ,  
 containing 5 weight per cent of the vinyl ether. The reaction mixture was refluxed for 4 hours. The copolymer was then washed with water to remove excess base. Infrared analysis indicated complete neutralization of the  $-\text{SO}_2\text{F}$  groups to  $-\text{SO}_3\text{Na}$  groups. The resulting resin could be molded into tough clear films.

**EXAMPLE XII**

Using the procedure of Example XI, a 2-4 mil film of a copolymer of tetrafluoroethylene and

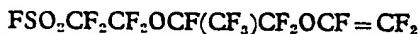
- 15  $\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF} = \text{CF}_2$   
 20 was placed in refluxing NaOH-methanol. The resultant film was clear and contained  $-\text{SO}_3\text{Na}$  groups as indicated by infrared analysis.

**EXAMPLE XIII**

- 25 The coagulated tetrafluoroethylene copolymer of Example X was washed with one liter of 10 per cent HCl in portions. The resultant resin was then washed with water to remove excess acid. Infrared analysis indicated essentially complete conversion of the  $-\text{SO}_3\text{Na}$  groups to  $-\text{SO}_3\text{H}$  groups.

**EXAMPLE XIV**

- 30 Into a platinum lined shaker tube were charged 2 g of an eight week per cent copolymer of a vinyl ether having the formula



- 35 with tetrafluoroethylene and 10 g of  $\text{NH}_3$ . The reaction mixture was agitated for 4 hours under autogenous pressure at a temperature of 40  $100^\circ\text{C}$ . Infrared analysis of the resultant copolymer indicated essentially complete formation of  $-\text{SO}_2\text{NH}_2$  groups from the  $-\text{SO}_2\text{F}$  groups.

**EXAMPLE XV**

- 45 Into a Carius tube were charged 0.75 g of a vinyl ether having the formula



- 50 and 20 ml of perfluorodimethylcyclobutane. The mixture was frozen, the tube evacuated and 2 g of tetrafluoroethylene edded. About 30 cc, at atmospheric pressure, of 2.4%  $\text{N}_2\text{F}_2$  in  $\text{N}_2$ , was injected and polymerization was carried out at room temperature in the sealed

tube for a period of 24 hours. A copolymer of the vinyl ether and tetrafluoroethylene was obtained.

**EXAMPLE XVI**

To 400 ml of water was added 7 g of a copolymer of tetrafluoroethylene and perfluoro-[2 - (2 - fluorosulfonylethoxy) propyl vinyl ether] and 6 g of triethylamine. The reaction mixture was refluxed for 96 hours. The  $-\text{SO}_2\text{F}$  groups of the copolymer were substantially completely converted to  $-\text{SO}_3\text{NH}_2$  groups.

**EXAMPLE XVII**

55 Into a horizontal autoclave of 2 gallon capacity is charged 1 liter of deoxygenated distilled water, 5 g of ammonium perfluorocaprylate, and 239 g of perfluoro[2 - (fluorosulfonylethoxy)propyl vinyl ether]. The free space of the autoclave is evacuated and filled with gaseous tetrafluoroethylene. The mixture is stirred with horizontal paddles at 105 RPM and heated to  $85^\circ\text{C}$ . The tetrafluoroethylene pressure is adjusted to 50 psig. A solution of 1 g of ammonium persulfate in 500 ml of water is pumped into the reactor followed by 250 ml of water to purge the pump and injection line. Tetrafluoroethylene is supplied to maintain the pressure at 50 psig during the polymerization period. After 71 minutes of polymerization the mixture is cooled and removed from the reactor. Two liquid phases are obtained, the upper phase being an aqueous dispersion of copolymer and the lower phase being an aqueous dispersion of copolymer and the lower phase being the unreacted perfluoroether.

60 The upper layer is separated and coagulated by high speed stirring to give 294 g of copolymer containing 17 weight per cent perfluoro-[2 - (2 - fluorosulfonylethoxy)propyl vinyl ether].

**EXAMPLE XVIII**

65 A 400 ml Hastelloy C (trade mark) shaker tube was flushed with nitrogen and charged successively with a solution of 0.20 g of ammonium perfluorooctanoate (Fluorochemical FC-126, Minnesota Mining & Mfg. Co.) in 250 ml of deoxygenated distilled water; 1.00 g of potassium persulfate; and 2.4 g of perfluoro[2 - (2 - fluorosulfonylethoxy) - propyl vinyl ether]. The tube was immediately closed, chilled to  $-78^\circ\text{C}$ , evacuated, and then charged successively with 14.5 g of perfluoro(methyl vinyl ether) and 6.5 g of tetrafluoroethylene. The tube was shaken at  $60^\circ\text{C}$  for 4 hours.

70 After cooling the tube and venting the unreacted gaseous monomers, the tube was opened and a liquid latex-like product was discharged. This was washed twice with approximately 50 ml for each washing of 1,1,2 - trichloroperfluoroethane to remove unreacted, non-volatile fluorosulfonyl monomer and then coagulated by freezing. The polymeric product was separated

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- from the aqueous phase by filtration and macerated in a high-speed mixer with water to remove electrolytes. The resulting wet polymer was vacuum - dried for 80 hours at 25°C under a pressure of 0.1 mm mercury. The weight of the dried terpolymer of perfluoromethyl vinyl ether, tetrafluoroethylene and perfluoro[2 - (2 - fluorosulfonylethoxy) - propyl vinyl ether] was 8.3 grams.
- 10 The infrared absorption spectrum of a thin film of the polymeric product was measured. An absorption band at 11.27 $\mu$  indicated the presence of the  $-\text{OCF}_3$  group and absorption bands at 6.80 $\mu$  and 10.15 $\mu$  indicated the presence of the  $-\text{SO}_2\text{F}$  group. Absorption bands attributed to fluorine attached to carbon were also present.
- 15 One hundred parts by weight of the terpolymer were mixed with 20 parts by weight of litharge on a two-roll rubber mill. The mix was removed from the mill and shaped and cured in the form of a film approximately 1 mm thick by pressing it at 125°C for 30 minutes between the heated platens of a hydraulic press. The cured film exhibited an elongation at break of 150 per cent and a permanent set at break of about 5 per cent. It was insoluble in perfluorodimethylcyclohexane whereas the uncured terpolymer was soluble.

## EXAMPLE XIX

A 400 ml Hastelloy shaker bomb is swept with nitrogen and charged with 200 ml of deoxygenated distilled water, 3.0 g (11.0 mmoles) of disodium phosphate heptahydrate, 0.25 g (2.4 mmoles) of sodium bisulfite, 0.15 g (0.3 mmole) of ammonium perfluoroctanoate, and 5.0 g (11.0 mmoles) of perfluoro[2 - (2-vinylxyloxy - 1 - methylethoxy)-ethane sulfonyl] fluoride. The bomb is closed, cooled to -80°C, and purged of oxygen by evacuating to one millimeter pressure of mercury. With the interior under reduced pressure, 17.3 g (0.115 mole) of hexafluoropropene and 27.5 g (0.43 mole) of vinylidene fluoride are introduced. The bomb is shaken and the temperature inside the reaction chamber is increased to 60°C and held there for two hours. The bomb is then cooled to room temperature, and excess gaseous reactants vented to the atmosphere. The partially coagulated product is removed. Coagulation is completed by freezing. The polymer is isolated by filtration, washed thoroughly with water, and dried overnight at 70°C in a vacuum oven. The dry white polymer weighed 31.2 g. Analysis for carbon, hydrogen, fluorine and sulfur showed that the product contains 33.1 per cent C; 2.1 per cent H; 63.4 per cent F and 0.8 per cent S.

40 The polymer is compounded on a two-roll rubber mill at 25°C to contain the following:

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The product is compounded on a two-roll rubber mill to contain the following:

Parts by Weight
Terpolymer
Carbon Black, Medium Thermal
MgO
PbO

This compounded stock is vulcanized by pressing sheets in a mold for 30 minutes at 150°C followed by removing the sheets and heating them in an air oven for 24 hours at 204°C.

The following physical properties were measured at 21.1°C:

Tensile strength, psi	1625
Elongation at break, per cent	340
Stress at 200 per cent elongation, psi	1175

## EXAMPLE XX

A 400 ml Hastelloy shaker bomb is swept with nitrogen and charged with 200 ml of deoxygenated distilled water, 3.0 g (11 mmoles) of disodium phosphate heptahydrate, 0.55 g (2.4 mmoles) of ammonium persulfate, 0.15 g (0.3 mmole) of ammonium perfluoroctanoate, 0.25 g (2.4 mmoles) of sodium bisulfite, and 2.5 g (6.0 mmoles) of perfluoro[2 - (2 - vinyloxy - 1 - methylethoxy) - ethane sulfonyl] fluoride. The bomb is closed, cooled to -80°C, and purged of oxygen by evacuating to one millimeter pressure of mercury. With the interior under reduced pressure 17.3 g (0.115 mole) of hexafluoropropene and 27.5 g (0.43 mole) of vinylidene fluoride are introduced. The bomb is shaken and the temperature inside the reaction chamber is increased to 60°C and held there for two hours. The bomb is then cooled to room temperature, and excess gaseous reactants vented to the atmosphere. The partially coagulated product is removed. Coagulation is completed by freezing. The polymer is isolated by filtration, washed thoroughly with water, and dried overnight at 70°C in a vacuum oven. The dry white polymer weighted 31.2 g. Analysis for carbon, hydrogen, fluorine and sulfur showed that the product contains 33.1 per cent C; 2.1 per cent H; 63.4 per cent F and 0.8 per cent S.

The polymer is compounded on a two-roll rubber mill at 25°C to contain the following:

Parts by Weight
Terpolymer
Carbon Black, Medium Thermal
MgO
Hexamethylene diaminecarbamate

A portion of this compounded stock is pressed in a mold for 30 minutes at 100°C to form a sheet. The resulting vulcanizate has a tensile strength at the break of 1275 psi and an elongation at the break of 160 per cent.

Another portion of this compound stock is

pressed in a mold for 30 minutes at 100°C to form a sheet. The sheet is removed from the mold, and is then heated in an oven to 204°C over a four hour interval and held to that temperature for 24 hours. The resulting vulcanizate has the following physical properties measured at 21.1°C:

Tensile at break, psi.	2350
Elongation at break, per cent	300
10 Stress at 200 per cent elongation, psi	1725

#### EXAMPLE XXI

A 400 ml stainless steel shaker tube is swept with nitrogen and charged with 100 ml of deaerated distilled water, 0.3 gm of ammonium perfluorooctanoate, 0.95 gm of potassium persulfate, 2.5 gm of disodium hydrogen phosphate heptahydrate, 0.2 gm of sodium sulfite, and 3.03 gm (.0068 mole) of perfluoro[2-(2-vinyloxy - 1 - methylethoxy) ethane sulfonyl]fluoride. The tube is closed, cooled in Dry Ice/acetone and evacuated to one millimeter of mercury pressure. To the evacuated tube is then introduced 34.2 gm (.206 mole) of perfluoro(methyl vinyl ether), followed by 12.7 gm (.127 mole) of tetrafluoroethylene. The shaker tube is heated and agitated for 8 hours at 50°C. The latex formed by the reaction is coagulated by freezing in a Dry Ice/acetone bath. After warming to room temperature, the solid polymer is separated by filtration and washed thoroughly with water to remove soap

and inorganic salts. The polymer is dried in a hood at room temperature for 2 days, followed by a few minutes milling on a 2-roll rubber mill at 100°C to remove any remaining water. The inherent viscosity of a 0.1 per cent solution of the polymer in 2,3 - dichloroperfluorobutane at 30°C is 1.15 with 80 per cent of the polymer being soluble. Infrared spectra analyses on pressed films of 1—2 mil thickness show that the polymer contains about 37 mole per cent of perfluoro(methyl vinyl ether) and about 0.8 mole per cent of perfluoro[2 - (2 - vinyloxy - 1 - methylethoxy)ethane sulfonyl]fluoride. After heating the polymer in an oven at 288°C there is a weight loss of 2.1 per cent after 100 hours and 8.7 per cent after 585 hours.

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One hundred parts of a copolymer prepared according to the method of Example XXI is compounded on a 2-roll rubber mill with 20 parts of litharge and 20 parts of medium thermal carbon black. The composition is sheeted off the mill and vulcanized into various test specimens by heating for 30 minutes at 175°C under pressure in a mold (removing the formed parts from the mold and then heating them at atmospheric pressure, by gradually raising the temperature to 204°C over a 12 hour period, followed by treatment at 204°C for 24 hours more. The following physical properties are obtained:

65	Tensile strength—psi at 25°C	1570
	Per cent elongation at break at 25°C	260
	Per cent permanent set at 25°C	12
	ASTM: D676-59T hardness (Duro A) at 25°C	76
	ASTM: D675-59T hardness (Duro A) at 100°C	65
	ASTM: D945-59 resilience at 25°C	19
70	ASTM: D945-59 resilience at 100°C	61
	ASTM: D395-61 compression set at 121°C	86
	Temperature where torsional stiffness is 10,000 pounds per square inch	—4.44°C

EXAMPLE XXIII

75 A. A polymer containing the three monomers of Example XXI is prepared, wherein the concentration of perfluoro(methyl vinyl ether) is about 36 mole per cent, and the concentration of perfluoro[2 - (2 vinyloxy - 1 - methylethoxy)ethane sulfonyl]fluoride is about 0.21 mole per cent. After heating the polymer at 288°C for 327 hours there is a weight loss of 3.4 per cent.

90

B. On a 2-roll rubber mill 100 parts of the polymer from A is compounded with 20 parts of magnesium oxide. Test specimens are prepared by vulcanizing the composition for 30

minutes at 175°C under pressure in a mold, removing the formed parts from the mold and then heating them at atmospheric pressure by gradually raising the temperature to 204°C over a 12 hour period, followed by treatment at 204°C for 24 hours more.

95

C. The procedure of B is followed, except magnesium oxide is replaced by calcium oxide.

D. The procedure of B is followed except magnesium oxide is replaced by litharge, and 20 parts of medium thermal carbon black is added.

The above elastomer compositions have the following physical properties:

100

	B	C	D
Tensile strength at 25° C. — psi.	2600	2540	1910
Per cent elongation at break at 25° C.	240	240	290
Per cent permanent set at break	10	35	7
Per cent weight loss at 288° C. after 20 hours	0.7	1.0	—
Per cent weight loss at 288° C. after 89 hours	1.3	1.9	—

## EXAMPLE XXIV

On a 2-roll rubber mill 100 parts of the polymer of Example XXIII "A" is compounded with 10 parts of "Maglite" Y magnesium oxide and 1 part of ethylenediaminecarbamate. Test sheets are prepared by vulcanizing the composition according to the procedure of Example XXIII "B". The following physical properties are obtained:

Tensile strength—psi at 25°C	3360
Tensile strength—psi at 100°C	740
Per cent elongation at break at 25°C	240
Per cent elongation at break at 100°C	180
Per cent permanent set at break at 25°C	7
Per cent permanent set at break at 100°C	4
Temperature when torsional stiffness is 10,000 pounds per square inch	-1°C

## EXAMPLE XXV

20 A. A polymer containing the three monomers of Example XXI is prepared wherein the concentration of perfluoro(methyl vinyl ether) is about 38 mole per cent and the concentration of perfluoro[2 - (2 - vinyloxy - 1 - methyl-ethoxy) ethane sulfonyl]fluoride is about 0.38 mole per cent. After heating for 186 hours at 288°C, the weight loss is 2.2 per cent.  
 B. On a 2-roll rubber mill, 100 parts of the polymer from A is compounded with 10 parts of "Maglite" Y magnesium oxide; 20 parts of medium thermal carbon black and 1 part of ethylenediaminecarbamate. Test sheets are prepared by vulcanizing the composition according to the procedure of Example XXIII "B". The following physical properties are obtained:

Tensile strength—psi at 25°	2640
Tensile strength—psi at 100°C	1000
Per cent elongation at break at 25°C	140
Per cent elongation at break at 100°C	80
Per cent permanent set at break at 25°C	1
Per cent permanent set at break at 100°C	1
Temperature where torsional stiffness is 10,000 pounds per square inch	-3°C

45 Per cent weight increase after 7 days immersion at 23.9°C in:

Acetone	2
Ethyl acetate	1
Toluene	1
Methylene chloride	1
Chloroform	1
Pyridine	0
Dimethyl formamide	1
Tetrahydrofuran	1
70 per cent nitric acid	8
"Freon" (trade mark) F-113	36

While in the foregoing examples we have only exemplified the preparation of certain of the novel fluorocarbon ethers and polymers thereof according to the invention, it will be apparent to those skilled in the art that fluorocarbon ethers of the above-mentioned formula, that is



where R<sub>1</sub> is a perfluoroalkyl radical containing from 1 to 10 carbon atoms, those of the said formula where Y is fluorine, those of the said formula where n is 3, and those of the said formula where two or more of R<sub>1</sub>, Y and n have the said meanings, and comparable to those exemplified by appropriate choice of starting materials.

## WHAT WE CLAIM IS:—

1. A fluorocarbon ether having the general formula



where R<sub>1</sub> is fluorine or a perfluoroalkyl radical having from 1 to 10 carbon atoms, Y is fluorine or a trifluoromethyl radical, n is 1, 2 or 3, and M is fluorine, a hydroxyl radical, an amino radical or a radical having the formula —OMet where Met is an alkali metal or a substituted or unsubstituted ammonium radical.

2. The fluorocarbon ether of the formula



3. The fluorocarbon ether of the formula

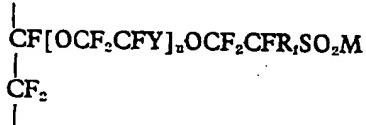


4. A method of preparing a fluorocarbon vinyl ether according to claim 1 in which M is fluorine, which comprises pyrolysing a fluorocarbon ether of the formula



where R<sub>i</sub>, Y and n have the meanings specified in claim 1, and A is —COR or —COOX, X being an alkali metal, at a temperature of from 180° to 600°C.

5. A polymeric material containing the structure



15 where R<sub>i</sub> is fluorine or a perfluoroalkyl radical having from 1 to 10 carbon atoms, Y is fluorine, a hydroxyl radical, an amino radical or a radical of the formula —OMet where Met is an alkali metal or a substituted or unsubstituted ammonium radical.

20 6. The homopolymer of a fluorocarbon vinyl ether as claimed in Claim 1.

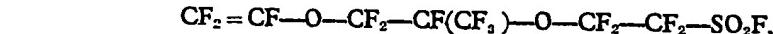
7. The homopolymer of the vinyl ether of the formula



25 8. The homopolymer of the vinyl ether of the formula



the halogenated ethylene is vinylidene fluoride and the perfluorinated alphaolefin is hexa-fluoropropylene.



the halogenated ethylene is tetrafluoroethylene, and the third monomer is a perfluoro(alkyl vinyl ether).

65 16. A copolymer according to claim 15, wherein the perfluoro(alkyl vinyl ether) is perfluoro(methyl vinyl ether).

70 17. An aqueous dispersion in which the dispersed particles are formed of a polymer as claimed in any of claims 5 to 16.

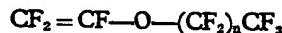
18. A method of preparing a polymer of a vinyl ether of the formula



where R<sub>i</sub>, n and Me have the meanings specified in claim 1, which comprises polymerizing



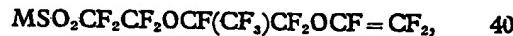
9. A copolymer of a fluorocarbon vinyl ether as claimed in Claim 1, ethylene or a halogenated ethylene, and at least one monomer which is a perfluorinated alpha-olefin or a perfluoro(alkyl vinyl ether) of the formula



where n is 0 to 5.

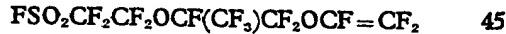
10. A copolymer according to Claim 9, wherein R<sub>i</sub> is fluorine.

11. A copolymer of the vinyl ether of the formula



where M has the meaning stated in Claim 1 and tetrafluoroethylene.

12. A copolymer of the vinyl ether of the formula



and tetrafluoroethylene.

13. A copolymer of a vinyl ether of the formula



where Met is an alkali metal or a substituted or unsubstituted ammonium radical, and tetrafluoroethylene. 50

14. A copolymer according to claim 10, wherein the vinyl ether is

15. A copolymer according to claim 10, wherein the vinyl ether is 60



where R<sub>i</sub>, Y and n have the meanings specified in claim 1, which comprises polymerizing said vinyl ether in a perfluorinated liquid solvent in the presence of a perfluorinated free radical initiator. 75

19. A method of preparing a polymer of a vinyl ether of the formula 80

85

20. A method of preparing a polymer of a vinyl ether of the formula  
 $\text{FSO}_2\text{CFR}_1\text{CF}_2\text{O}[\text{CFYSF}_2\text{O}]_n\text{CF}=\text{CF}_2$ ,  
5 where  $R_1$ , Y and n have the meanings specified in claim 1 which comprises polymerizing said vinyl ether in contact with an aqueous liquid phase and in the presence of a free radical initiator.  
10 21. A process for the preparation of a fluorocarbon ether according to claim 1 sub-
- stantially as herein described in any of Examples I to V.  
22. A process for the preparation of a polymer according to claim 5 substantially as herein described in any of Examples VI to XXV. 15

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